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Diaquabis[4-(dimethylamino)benzoato-κ*O*]-(nicotinamide-κN^1)manganese(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.005 Å
R factor = 0.072
wR factor = 0.190
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

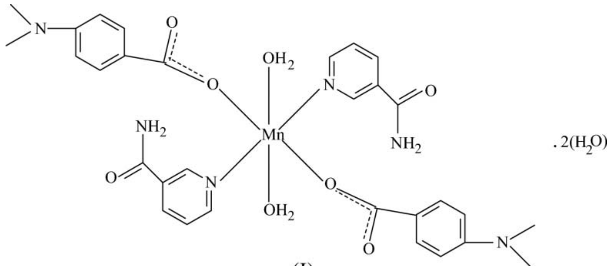
The title manganese complex, $[Mn(C_9H_{10}NO_2)_2(C_6H_6N_2O)_2(H_2O)_2]\cdot 2H_2O$, is monomeric and centrosymmetric. It contains two 4-(dimethylamino)benzoate (DMAB) and two nicotinamide (NA) ligands, two coordinated and two uncoordinated water molecules, all ligands being monodentate. The four O atoms in the equatorial plane around the Mn atom form a slightly distorted square-planar arrangement, while the distorted octahedral coordination is completed by the two NA N atoms in the axial positions. In the crystal structure, intermolecular O—H···O and N—H···O hydrogen bonds link the molecules to form a supramolecular structure.

Comment

Transition metal complexes with biochemical molecules show interesting physical and/or chemical properties, for which they may find applications in biological systems (Antolini *et al.*, 1982). 4-Aminobenzoic acid has been extensively reported in coordination chemistry, as a bifunctional organic ligand, due to the varieties of its coordination modes (Chen & Chen, 2002; Amiraslanov *et al.*, 1979; Hauptmann *et al.*, 2000). Nicotinamide (NA) is one form of niacin and a deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974).

The structural functions and coordination relationships of the arylcarboxylate ion in Mn^{II} complexes of benzoic acid derivatives may also change, depending on the nature and position of the substituent groups on the benzene ring, the nature of the additional ligand molecule or solvent, and the medium of synthesis, as in Co^{II} complexes (Nadzhafov *et al.*, 1981; Shnulin *et al.*, 1981; Antsyshkina *et al.*, 1980; Amiraslanov *et al.*, 1979; Adiwidjaja *et al.*, 1978).

The structure determination of the title compound, (I), was undertaken in order to determine the properties of the DMAB and NA ligands and also to compare the results obtained with those reported previously.


(I)

Complex (I), with the Mn atom on a centre of symmetry, contains two DMAB and two NA ligands, as well as two

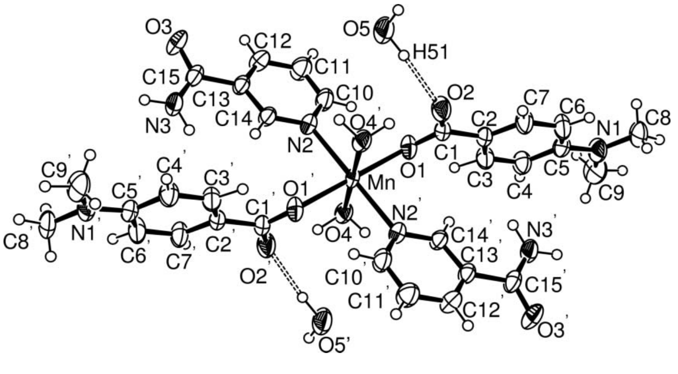


Figure 1
The molecular structure of (I) with 50% probability displacement ellipsoids (arbitrary spheres for H atoms). Hydrogen bonds are shown as double dashed lines. Primed atoms are generated by the symmetry operation ($-x$, $-y$, $-z$).

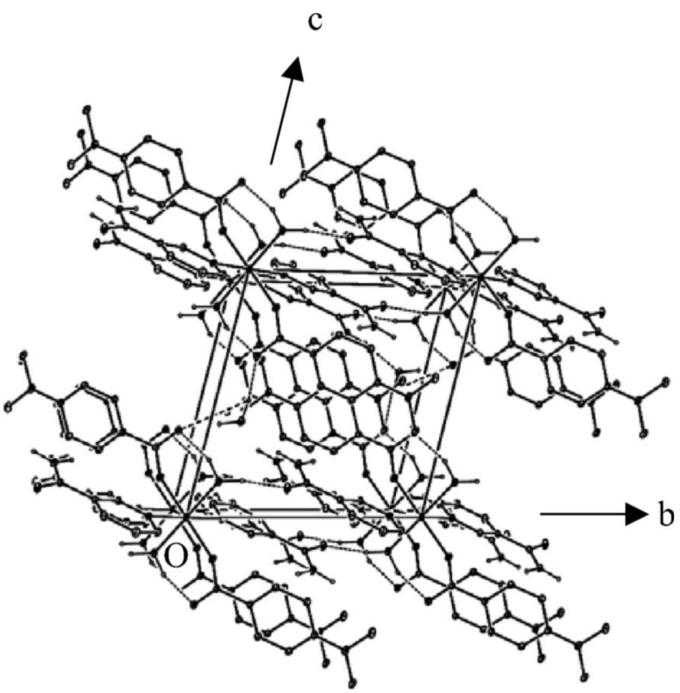


Figure 2
A packing diagram of (I), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

coordinated and two uncoordinated water molecules (Fig. 1). All ligands are monodentate. The four symmetry-related carboxylate and water O atoms (O1, O4 and the symmetry-related atoms, O1′, O4′) in the equatorial plane around the Mn atom form a slightly distorted square-planar arrangement, while the slightly distorted octahedral coordination is completed by the two N atoms of the NA ligands (N2 and the symmetry-related atom N2′) in the axial positions (Fig. 1).

The near equality of the C1—O1 and C1—O2 bonds (Table 1) in the carboxylate group indicates a delocalized bonding arrangement, rather than localized single and double bonds, as in bis(4-hydroxybenzoato-*κO*)bis(nicotinamide-*κN*)zinc(II) (Necefoğlu *et al.*, 2002) and tetraaquabis[4-(dimethylamino)benzoato-*κO*]manganese(II) dihydrate (Hökelek & Necefoğlu, 2007). This may be due to the intra- and intermolecular O—H⋯O hydrogen bondings of the carboxylate O atoms (Table 2). The Mn atom is displaced out of the least-squares plane of the carboxylate group (O1/C1/O2) by 0.968 (1) Å. The dihedral angle between the planar carboxylate group and the benzene ring *A* (C2–C7) is 3.45 (28)°, while the dihedral angle between rings *A* and *B* (N2/C10–C14) is 77.35 (12)°.

As can be seen from the packing diagram (Fig. 2), the Mn atoms are located at the corners of the unit cell and the molecules of (I) are linked by intra- and intermolecular O—H⋯O and N—H⋯O hydrogen bonds (Table 2), to form a supramolecular structure.

Experimental

Compound (I) was prepared by the reaction of $MnSO_4$ (1.51 g, 10 mmol) and NA (2.44 g, 20 mmol) in H_2O (100 ml) with sodium *p*-dimethylaminobenzoate (3.74 g, 20 mmol) in H_2O (100 ml) at room temperature. The mixture was filtered and set aside to crystallize at ambient temperature for several days, giving yellow single crystals of (I).

Crystal data

$[Mn(C_9H_{10}NO_2)_2(C_6H_6N_2O)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 699.62$
Triclinic, $P\overline{1}$
$a = 8.1979$ (2) Å
$b = 10.0888$ (2) Å
$c = 10.2559$ (3) Å
$\alpha = 76.465$ (2)°
$\beta = 88.984$ (3)°
$\gamma = 77.442$ (3)°
$V = 804.46$ (4) Å^3
$Z = 1$
Cu $K\alpha$ radiation
$\mu = 3.90$ mm^{-1}
$T = 294$ (2) K
0.30 × 0.28 × 0.13 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.362$, $T_{max} = 0.602$
3375 measured reflections
3186 independent reflections
2724 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.072$
$wR(F^2) = 0.190$
$S = 1.06$
3186 reflections
264 parameters
8 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 1.38$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.105 (2)	O1—C1	1.272 (4)
Mn—O4	2.224 (2)	O2—C1	1.263 (4)
Mn—N2	2.295 (3)		
O1^i—Mn—O4	89.45 (9)	O1—Mn—N2	91.34 (10)
O1—Mn—O4	90.55 (9)	O4^i—Mn—N2	92.26 (10)
O1^i—Mn—N2	88.66 (10)	O4—Mn—N2	87.74 (10)

Symmetry code: (i) $-x$, $-y$, $-z$.

Table 2

Table 1. Hydrogen-bond geometry (Å, °)..

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H51$\cdots$O2	0.97 (5)	1.96 (6)	2.917 (4)	169 (7)
O5—H52$\cdots$O2^{ii}	0.93 (5)	1.94 (5)	2.861 (4)	171 (7)
O4—H41$\cdots$O2^{iii}	0.98 (3)	1.82 (4)	2.757 (4)	159 (3)
O4—H42$\cdots$O3^{iv}	0.94 (2)	1.83 (2)	2.751 (4)	166 (3)
N3—H31$\cdots$O5^{v}	0.92 (5)	1.98 (5)	2.883 (4)	170 (5)

Symmetry codes: (ii) $-x, -y, -z+1$; (iii) $-x, -y, -z$; (iv) $x, y-1, z$; (v) $-x, -y+1, -z$.

The highest peak and deepest hole in the final difference electron density map are located 0.99 and 0.85 Å, respectively, from the Mn atom. H11, H14 and methyl H atoms were positioned geometrically with C—H = 0.93 and 0.96 Å, for aromatic (H11 and H14) and methyl H atoms, respectively, and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = xU_{\rm eq}({\rm C})$, where $x = 1.2$ for aromatic and $x = 1.5$ for methyl H atoms. The remaining H atoms were located in difference syntheses and refined isotropically [O—H = 0.92 (5)–0.983 (18) Å and $U_{\rm iso}$(H) = 0.045 (11)–0.13 (3) Å^2 (for OH$_2$); N—H = 0.92 (5) and 0.95 (5) Å and $U_{\rm iso}$(H) = 0.052 (12) and 0.067 (15) Å^2 (for NH$_2$); and C—H = 0.88 (6)–1.08 (5) Å and $U_{\rm iso}$(H) = 0.040 (10)–0.083 (18) Å^2 (for aromatic CH)].

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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